Magnesium/Air combustion at pilot scale and subsequent PM and NO_x emissions

Patxi Garra¹, Gontrand Leyssens¹, Olivier Allgaier¹, Cornelius Schönnenbeck¹, Valérie
Tschamber¹, Jean-François Brilhac^{1,*}, Toni Tahtouh², Olivier Guézet², Sylvain Allano²

¹Laboratoire Gestion des Risques et Environnement (EA2334), Université de Haute Alsace,
3bis rue Alfred Werner, 68200, Mulhouse, France

²PSA Peugeot Citroën, Centre Technique de Vélizy, Route de Gisy, 78943 Vélizy Villacoublay
Cedex, France

corresponding author :

jean-francois.brilhac@uha.fr

co-authors emails

patxi.garra@uha.fr, gontrand.leyssens@uha.fr, olivier.allgaier@uha.fr,
cornelius.schonnenbeck@uha.fr, valerie.tschamber@uha.fr, jean-francois.brilhac@uha.fr,
toni.tahtouh@mpsa.com, olivier.guezet@mpsa.com, sylvain.allano@mpsa.com

submitted in revised form to
Applied Energy(ELSEVIER)

Abstract

Fossil fuel scarcity, global warming and non-constant energy production through renewable energies (wind turbines and photovoltaic cells for example), lead to investigate innovative energy sources and new ways for energy storage. In the present study, magnesium powder has been considered as a new possible energy source. In order to analyze more deeply the magnesium combustion and the generated by-products, short time stable magnesium/air flames have been realized in a combustion chamber using an oxy-acetylene flame for ignition. Sieved magnesium samples with two fractions were combusted: 20-50 μm and 50-70 μm . The power delivered by the Mg/air flame was estimated in the range 3- 5 kW. The gaseous emissions (O_2 , CO_2 from oxy-acetylene combustion, NO and NO_2) were analyzed with on-line analyzers and the particulate emissions were analyzed with an Electrical Low Pressure Impactor (ELPI). The mass concentration of emitted particles whose size is smaller than 10 μm was proved to be very high (up to 35 g/Nm^3) and the emitted particles were mainly bigger than 1 μm (84 to 97 wt%). NO_x emissions were higher for the 20-50 μm Mg fraction (NO average of $4300 \pm 200 \text{ mg}/\text{Nm}^3$) than for the 50-70 μm Mg fraction (NO average of $1100 \pm 140 \text{ mg}/\text{Nm}^3$).

Keywords:

Magnesium combustion, Energy storage, Particulate Matter (PM), Electrical Low Pressure Impactor (ELPI), Nitrogen Oxides (NO_x)

Graphical abstract

Highlights

- The feasibility of magnesium energy release at a pilot scale (from 3.0 to 5.0 kW) is demonstrated.
- Magnesium/air stable flames are obtained from raw magnesium powder and combustion completion ratios ranges from 91 to 100 %.
- Total suspended particles (TSP) emissions, estimated from ELPI measurements, ranges from 1 to 35 $\text{g}/(\text{N})\text{m}^3$
- NO_x emissions are higher for the 20-50 μm fraction than for the 50-70 μm fraction (NO average of $1100 \pm 140 \text{ mg}/(\text{N})\text{m}^3$).

Introduction

Fossil fuel scarcity and global warming lead to diversification of the energy sources. The main goals for new energy production and storage consist in limiting greenhouse gases emissions such as CO₂, in promoting renewable energies and limiting their environmental impacts. Renewable energy sources have known downsides. For instance, wind turbines [1–3] or photovoltaic cells [4,5] present non-constant energy production and release. Therefore innovative ways to perform energy storage and production have to be investigated. Among such innovative ways are production of sustainable biofuels using a great variety of resources that do not compete with edible crops and new conversion technologies. An example is hydrogen (H₂) energy storage using electrolyzers [6] and release in fuel cells [7,8] for vehicle applications or production of a totally renewable biodiesel through supercritical triglycerides ethanolyse [9].

Most of the renewable energy sources depends on environmental conditions such as solar and wind and are not portable. Energy storage is then a key issue concerning a transition towards zero-carbon systems. Energy storage in a chemically reduced form for subsequent combustion and energy release is a valuable option. In this context metal particles could be considered as a renewable energy carrier [10].

The investigations of energy storage using metal powder are scarce [11] and mainly aluminum and magnesium are considered as a metal candidate for such an application. Magnesium is currently the 8th most abundant element in the earth's crust with 2.1 wt% [12]. Its electrolysis is already widely documented in order to obtain metal Mg from Mg oxides [13]. Many studies consider magnesium combustion under different combustion atmospheres, among which are carbon dioxide at low pressure [14], water vapour [15] and O₂-inert atmosphere [16]. Fundamental researches on burning processes and mechanisms are also widely referenced [16–19]. The ignition and burning of metal particles were investigated by many authors from the nineteen-sixties [20,21] until today [11,22,23]. The investigations considered micron-sized metal particles or nano-sized particles [24] exhibiting shorter burning times. Magnesium combustion is mainly used in punctual energy release applications, for example in nano-thermites pyrotechnics [24], mixed with aluminum building alloys for welding applications [25–27] or for space rockets [28–31]. But these applications are currently not considered as potentially interesting for magnesium-based energy storage, as they do not involve a steady continuous release of energy through magnesium combustion and the products, i.e. magnesium oxide, are released into the atmosphere.

Recently, the direct combustion of recyclable metal fuels has been thoroughly considered [32]. Metal particles exhibit energy density similar to liquid hydrocarbons making them relevant for transportation systems. Metal particles seem compliant with an external combustion engine. This vector is expected to be safer for the on-board storage compared to hydrogen commonly considered as the new energetic vector for mobility [33,34]. Another advantage of metal as an energy vector is its ability to be reduced; the oxide produced from combustion can be recycled using primary energy in a separate process. Consequently an essential requirement for the combustion of metal fuels is the complete capture of all the metal oxide formed [32]; solid combustion-product morphology and size have to be investigated on metal-fuelled burners. Since particulate matter emissions (PM) is an important issue for nowadays societies [35], fine (<1 µm) and ultrafine (<100 nm) particulate matters are especially pointed out as they can penetrate the deepest part of the lungs [36]. Therefore PM emissions generated by metal combustion have to be considered. Emissions of Nitrogen Oxides (NO_x) cause significant damage like smog formation, acid rain or ozone

formation at low altitudes [37]. The high flame temperature leads to high NO_x pollutant emissions [32] and this could be an issue for the development of the use of metal powders as a new energetic vector.

The future of energy generation for terrestrial applications could be the use of metal as fuel. However the pollutants emitted by the combustion of metal particles is not well documented in comparison to those emitted by the combustion of hydrocarbon fuels. The present study focuses on the magnesium combustion and the subsequent pollutants emitted. The metal recycling step - reduction of MgO to Mg using primary energy [32] as solar energy for instance [38] is out of the scope of this work. Two questions are then addressed: (i) what are the solid products of the combustion process occurring in a burning chamber with a continuous injection of Mg delivering a power suitable for use in automobile sectors? (ii) what are the pollutants emitted during the combustion process?

In order to investigate the efficiency of magnesium combustion and to analyze the by-products generated – including emissions of particulate matter and NO_x – stable magnesium/air flames have been produced in this study in a totally new laboratory scale combustion chamber. The power delivered by the Mg/air flame in this boiler has been estimated to be in the range 3 - 5 kW. This boiler is implemented in a combustion chamber. A cyclone allows trapping of particles in the chamber outflow. This enables the analysis of the solid and gaseous products emitted during the Mg/air reaction occurring in realistic situations. The gaseous emissions (O₂, NO and NO₂) are monitored using an online analyzer. The particulate emissions are analyzed with an Electrical Low Pressure Impactor (ELPI).

The experimental set-up is described in the first section of the paper. The second part of the paper presents mass and energy balances within such a combustion system. The evaluation of the combustion efficiency has been performed using innovative ways based on the thermogravimetric analysis of the residues produced by the combustion process, but also on the dynamic assessment of magnesium and O₂ consumption. NO_x and PM emissions are presented and discussed in the third part of the paper.

2. Material and methods

2.1. The combustion system

The magnesium powders used in this work are pure (>99.8%), supplied by Carl Roth® (France) as CP20.2 reference. The raw powder was sieved using a RETSCH GmbH (Germany) AS200 sifting machine. Two size fractions were studied: 20-50 µm and 50-70 µm. A scheme of the combustion system is depicted in figure 1. The system is composed of four main parts: magnesium aerosol generator, boiler, combustion chamber and cyclone. The nozzle inner diameter of the boiler is 22 mm; the combustion chamber diameter is 106 mm. The magnesium/air aerosol is generated using a PALAS GmbH (Germany) BEG 1000B device, allowing the injection of solid powder in the range 0.1-200 µm. Aerosol generation complies with norm VDI 3491 for reliable aerosol mass flow rate output. The combustion process may be decomposed in the following stages:

- setting air flow rates of the burner without magnesium particles injection,
- ignition of the oxy-acetylene flame in the combustion chamber,
- starting Mg powder injection at a small mass flow rate,
- increasing potentiometer of the PALAS to the nominal mass flow rate value for magnesium injection,
- stopping the oxy-acetylene flame once a stable Mg/Air flame is obtained,

- stopping the magnesium particles injection and immediate nitrogen inerting, from the solenoid valve releasing pressurized N₂, and stopping air injection in the combustion chamber.

The mass flow rate of magnesium ranges from 0.4 kg h⁻¹ for the 20-50 µm fraction to 0.8 kg h⁻¹ for the 50-70 µm fraction. The air mass flow rates are in the range 3 (N)m³ h⁻¹ - 3.5 (N)m³ h⁻¹.

Figure 1 : Scheme of the Mg/Air ignition and combustion process. EV=ON means that the solenoid valve is turned on during the inerting stop of the combustion, EV=OFF means that the solenoid valve is turned off during the combustion experiment.

The combustion lasted about 2 min, in order to limit the thermal abrasion of the combustion prototype. At the end of each experiment, the powders in the combustion chamber and also in the cyclone were collected which are thereafter denoted as residues. Morphological and chemical analyses of these residues were carried out.

Risks generated by the combustion process are mainly due to the high reactivity of Mg conditioned in a powder form. Considering the burner, the main hazard process is a flash back from the combustion chamber to the tank where fresh Mg is stored. To avoid such an undesirable event, the tank has to be immediately isolated from the combustion chamber in case of flash back. This is achieved in this combustion system by flushing the boiler with nitrogen. Considering the fuel itself, there is no significant toxicological risk except the ultrafine particle fraction since it can be inhaled and then interact with the lungs in the same way as other ultrafine particles. Nevertheless, metal in a pulverized form has to be handled carefully as it can produce an explosive atmosphere.

2.2. Fuel and residue characterizations

The particle size determination was performed using a Laser granulometer Scirocco 2000M from MALVERN® (λ=532 nm). Magnesium fuel and combustion residue were fed as powders in the granulometer. Results were obtained using the Fraunhofer method, the calculations being considered as valid for particles bigger than ten times the wavelength. Each sample was analyzed at least three times. Optical microscopy observations were performed using an OLYMPUS BX51 wide field microscope. For the different acquisitions, a 10X objective with a numerical aperture of 0.25 was used, having a lateral theoretical resolution of 1.5 µm. The fuel samples (fresh and oxidized) were analyzed using a thermogravimetric analyzer TA Instruments Q500.

2.3 Gaseous and particulate emissions assessment

Gaseous and particulate emissions were measured at the cyclone outflow, according to the European standard NF EN-304/A1 defined for biomass combustion exhaust

assessment. Figure 3 depicts the analytical system used. O₂, CO₂, NO and NO₂ outflows were measured using paramagnetic and infrared cells (Rosemount NGA 2000) and expressed in mg/(N)m³. A sample 1:10 Diluter 108 from JÜM Engineering was used for gas dilution at the entrance of the NO/NO₂ analyzer. The exact dilution factor (equal to 9.19 ±0.16) was determined passing NO spanning gas (from Air Liquide, France) in the diluted sampling line. An extended uncertainty for the NO_x concentrations takes into account the NO_x analyzer uncertainty and also the dilution uncertainty.

Figure 3: Experimental set-up for the characterization of the gaseous and particles emissions

An Electrical Low Pressure Impactor (ELPI) manufactured by DEKATI Ltd. (Tampere, Finland) was used to collect particles from 7 nm to about 10 µm into 12 size fractions. Inside the ELPI, the particles are first electrically charged, according to their Stokes diameter, then impacted on different stages, according to their inertia related to their aerodynamic diameter. A multistage electrometer counts the charged aerosol particles. The current induced is simultaneously measured for the twelve impactor stages, which is directly converted by the electrometer in particles numbers and concentrations using mathematical algorithms [39]. The number of particles depends on both the induced current measured at each stage and on the density of the particles in the exhaust gas. The aerosol from magnesium combustion is only composed of depleted air and MgO particles. A density of 3.6 g cm⁻³ for MgO is used in the ELPI software 4.10 to calculate particles number and mass concentration. The Total Suspended Particles (TSP from ELPI) are then estimated throughout the combustion experiments as well as the mass size distributions and number size distributions. In order to ensure that the collected particulate matter always remains below saturation, the exhaust gas was diluted at the ELPI entrance of exactly ten times, using a Dekati® FPS-4000 diluter.

3 – Results and discussions

3.1 Experimental runs

The mass flow rate of magnesium injected in the combustion chamber was accurately determined in order to estimate the mass balance in the reactor. The calibration of

magnesium injection depending on a PALAS potentiometer adjustment was done using a Retsch <5 µm nylon filter. Raw magnesium powder (Mg raw) was injected into the combustion chamber using an air carrier flow rate. Different potentiometer adjustments led to different injected magnesium masses. The calibration was performed considering the mass of magnesium injected during the time length of the experiment. The magnesium mass flow rate versus the potentiometer setting is plotted in figure 2. PALAS BEG 1000 aerosol generator meets the requirements of norm VDI 3491 and these results confirm the reliability of PALAS aerosol generators when injecting magnesium powder.

Figure 2: Calibration of the aerosol generator PALAS: mass flow rate of magnesium injected (kg s^{-1}), as a function of the PALAS potentiometer adjustment

A correction factor (denoted as X) may be estimated from the slope of the regression line: $X=0.255$ for Mg raw sample (see table 1). For the determination of the correction factors which may be associated to the other samples (Mg 20-50 µm and Mg 50-70 µm), the calibration was corrected by the apparent density of the different Mg fractions (table 1), according to the PALAS BEG 1000 operating manual. This apparent density was measured using a 1 mL graduated flask from Glasfirm®, see table 1. The standard deviation of the apparent density - RSD % based on five measurements - was used for the calculation of magnesium flow rate injection uncertainty.

Table 1: Average apparent densities of raw magnesium and of two sifted samples with size fractions 20-50 µm and 50-70 µm, and setting of PALAS equipment for each sample.

	Average apparent density (g/cm ³)	RSD % for average apparent density	PALAS correction factor X (X*Potentiometer=kg/h)
--	---	------------------------------------	--

		(based on five measurements)	
Mg raw	0.525	0.9	0.255 (calibration value)
Mg 20-50 μ m	0.505	1.4	0.245
Mg 50-70 μ m	0.532	1.0	0.258

A rectangular window (15 cm x 5 cm) allows observation of the flame near the burner in the combustion chamber. Pictures of the preliminary result combustion were taken using a 8-megapixel camera equipped with a filter consisting of traditional welding glasses with an UV and infrared radiation protection of factor 6.

A typical experimental run may be depicted through the four pictures presented in Figure 4. Figure 4.a corresponds to the first stage of the experiments, when only the blue oxy-acetylene flame occurs. Figure 4.b presents the flame once magnesium injection starts (20-50 μ m fraction in this run). The mass flow rate is progressively increased to reach the nominal flow rate (Figure 4.c) and the oxy-acetylene injection is stopped. At this time, Mg/Air flame emits strong luminous flashes. The magnesium flame is then considered as self-sustained (Figure 4.d). At this stage and for the rest of the run, it was not possible to get a more precise image of the Mg flame as the window is covered with MgO particles ejected from the flame and the radiative energy emitted is quite high.

Fig. 4a

Fig. 4b

Fig. 4c

Fig. 4d

Figure 4: Views of the flame, according to the successive stages of the combustion process: oxy-acetylene ignition (Fig. 4a), starting of the Mg combustion (Fig. 4b), stabilization of the Mg flame (Fig. 4c), self-sustained flame (Fig. 4d)

3.2 Characterization of raw and oxidized magnesium

The following chemical balance is assigned for magnesium combustion:

where $Mg_{(s)}$ and $MgO_{(s)}$ are the fresh and oxidized magnesium metal, respectively.

The molecular magnesium weight is equal to 24.3 g mol^{-1} and that of oxygen is 16.0 g mol^{-1} . According to equation (1) and to these values, the overall oxidation of the magnesium leads to a total mass gain of 65.8 %. Estimating the mass gain from fuel oxidization is therefore a valuable method to evaluate the extent of conversion of Mg in MgO. It allows the determination of the remaining amount of Mg (metal) in the collected residue that could be additionally oxidized.

Preliminary experiments were performed by TGA (TA Instruments Q500 thermogravimetric analyzer) to characterize the mass gain and the temperature range for Mg oxidation. Experiments were conducted from ambient temperature to 850°C at a heating rate of 10°Cmin^{-1} , under pure synthetic air flow of 3.6 (N)L h^{-1} (20 % O_2 , 80 % N_2).

The combustion completion was computed using a procedure inspired by the standard DIN EN 14961-2 (A1), which is usually intended to determine ash content of biomass fuels or residues. The samples (magnesium fuel or residue) were dried for 24h at 100°C (drying oven Memmert VM400) and weighed using a precision balance (Precisa XT 220A) in order to obtain the mass of the initial sample $m(\text{initial sample, dried})$. Then, a muffle furnace (Naberterm LT5/P330) was used to oxidize the magnesium metal (Mg) contained in the sample under a linear temperature ramp from ambient temperature to 815°C over 1 h and then maintaining 3 h at 815°C . The resulting residue was considered as MgO only and weighed and the corresponding mass is denoted $m(\text{sample}, 815^\circ\text{C})$. Each sample - residue or initial fresh fuel - was analyzed at least three times. The standard deviation of the mass gain was used to determine the uncertainty on the mass gain, which is defined through:

$$\% \text{mass gain} = 100 \frac{m(\text{sample}, 815^\circ\text{C}) - m(\text{initial sample, dried})}{m(\text{initial sample, dried})} \quad (2)$$

The mass gain allows characterization of the percentage of completion of the combustion reaction, which will be denoted as % combustion completion and which is the ratio between the mass gain from a residue that has undergone partial combustion and the maximum mass gain from the initial fuel:

$$\% \text{combustion completion} = 100 \left(1 - \frac{\% \text{mass gain}(\text{residue})}{\% \text{mass gain}(\text{initial fuel})} \right) \quad (3)$$

The volume size distributions of the two Mg fractions tested are available in figure 5, which demonstrate that magnesium sifting is not achieved accurately. For instance, particles bigger than $50 \mu\text{m}$ are observed in the Mg 20-50 μm sample. For the Mg 20-50 μm sample, the median volume size distribution is equal to $39.6 \mu\text{m}$, with only 10 vol% below $21.1 \mu\text{m}$ and 10 vol% above $70.0 \mu\text{m}$. For the 50-70 μm fraction, the median volume size distribution is equal to $60.4 \mu\text{m}$, with only 10 vol% below $30.8 \mu\text{m}$ and 10 vol% above $105.4 \mu\text{m}$.

Figure 5: Volume size distributions of the two magnesium sifted fractions used during the experiments

Oxidations under air of raw magnesium or of partially oxidized magnesium collected either in the combustion chamber or in the cyclone were performed by thermogravimetric analysis. The corresponding thermograms for fresh magnesium samples are given in figure 6, for the two investigated Mg fractions. The oxidation process occurs in two steps. First, a maximum mass gain up to 50% is observed around 600°C. Then a slower oxidation process occurs from 600 to 800°C. At 800°C, the Mg combustion is almost complete, with a mass gain of 63 wt% for Mg 50-70 μm and 55 wt% for Mg 20-50 μm. The final temperature (800°C) is higher than that (300 °C) which was proposed for the thermogravimetric analysis of magnesium oxidation under water [19]. But the oxidization mechanisms are different. The total mass gain obtained using TGA is slightly lower than the theoretical expected one (65.8 wt%) considering (1) and leads to the conclusion that some Mg particles present in the raw material are oxidized. This result is consistent with the microscope observation of the raw magnesium, as presented in figure 7. One may indeed observe marginal small crystals which might be MgO. These crystals are more abundant in the 20-50μm fraction. Similar results were obtained in Wang et al.'s work [19] where a mass gain of about 65% was obtained for the 43μm fraction (-325 mesh), but only about 57% for the 1-11μm fraction. Their Scanning Electron Microscopy microscope figures also exhibit small MgO crystals in the outer layer of Mg (metal).

Figure 6: Thermal behavior of the sifted Mg powder fraction under air at a heating rate of 10 K min^{-1}

Figure 7: Optical microscope image of raw magnesium fuel using Olympus BX51 microscope with a X10 objective

The volume size distributions of the residues collected in the combustion chamber during the combustion experiments (figure 8) exhibit a bimodal distribution. The first peak is centered at $42 \mu\text{m}$ for the $20\text{-}50 \mu\text{m}$ fraction (combustion experiments denoted as n°2 and n°3) and centered at $48 \mu\text{m}$ for the $50\text{-}70 \mu\text{m}$ fraction (combustion experiments n°5 and n°6). A second peak centered at $700 \mu\text{m}$ is observed. Strongly agglomerated particles could

produce this peak. A drying process and an ultrasonic agitation (300 rpm) were performed on this sample, but the agglomerated particles were not broken and dispersed after these processes. The presence of such agglomerated particles may be explained by the high temperature in the flame, thus promoting some strong bindings between MgO residues. In Wang et al's work [19], the authors indicated that temperatures for single Mg particles combustion are in the range 2000 - 3000 K. For the 20-50 μm range, the first peak is centered on 37 μm for the raw magnesium (see figure 5) and around 42 μm for the solid-oxide combustion product (see figure 8). Particles produced by combustion are then larger than initial magnesium particles due to the additional volume of oxygen gained during oxidation. Such a result also indicates that a heterogeneous combustion forming a porous oxide shell [32] around the magnesium particles may be the combustion mode prevailing in our combustion system. Even if magnesium is a candidate for vapour phase droplet combustion since its flame temperature exceeds its boiling point [19], the operating parameters such as the air/fuel ratio in the flame and the temperature may also influence the combustion mode [40].

Figure 8: Volume size distributions of the residues formed in the combustion chamber, during the experiments n°2, n°3, n°5 and n°6

The volume size distributions of the residues collected in the cyclone during the combustion experiments (figure 9) exhibit a unimodal distribution. A unique peak is indeed present close to 35 μm , corresponding to the ability of the cyclone to trap particles at the current gas velocity (cut-off diameter of the cyclone $d_{50}=6 \mu\text{m}$). Agglomerated particles around 700 μm are also marginally present in these residues.

Figure 9: Volume size distributions of the residues formed in the combustion cyclone during the combustion experiments n°2, n°3, n°5 and n°6.

Table 2 presents the mass gain measured from the different samples, either in the muffle furnace or using TGA. Whatever the experiment, the mass gain of residues collected in the combustion chamber is between 0.3 and 5.6 wt%, while that of residues collected in the cyclone is lower (0.2 to 4.0 wt%). The magnesium fuel injected and the residues collected are expressed in equivalent MgO for comparison in Table 3, where they are denoted as MgO injected and MgO collected, respectively. For the six experiments (n°1, n°2, n°3, n°5, n° 6 and n°7), the ratio between MgO collected and the equivalent MgO injected (table 3) ranges from 64.0 to 96.1%. It never reaches 100% because it is not easy to estimate the errors related to these measurements, as the whole MgO produced cannot be collected. A white MgO deposition was indeed observed in the sampling lines where it stuck. Hence, when recovering the residues, a small mass amount is surely left. Nevertheless, the percentage of MgO collected versus the equivalent MgO injected is quite satisfactory for six experiments: 64.0% (n°1, fraction 20-50 μm), 70.9 % (n°3, fraction 20-50 μm), 85.7 % (n°2 fraction 20-50 μm), 90.5 % (n°5, fraction 20-50 μm), 96.1 % (n°6, fraction 20-50 μm) and 94.9 % (n°7, fraction 20-50 μm). This percentage could be improved by trapping in a more efficient way the MgO particles before they stick, for instance using a multi-cyclones system. Longer combustion experiments (more than 2 min) would also probably ensure a better statistical reliability of the results.

Table 2: Thermal characterizations of magnesium fuel and of residues using a muffle furnace (mass gain during 3h at 815 °C) or a thermogravimetric analyzer (TGA, mass gain at 850°C after a heating rate stage at 10 K min⁻¹); subsequent completion of the combustion reaction.

Combustion test	Fuel/Chamber residue or Cyclone residue	Characterization technique	Mass gain (wt%)	Combustion completion (%)
n°1	Mg 20-50 μm	Muffle furnace	56.0 $\pm$ 1.0	
	Mg 20-50 μm	TGA	56.1 $\pm$ 0.9	
	Chamber residue	TGA	0.3 $\pm$ 0.2	99%
	Cyclone residue	TGA	0.2 $\pm$ 0,2	100%

n°2	Mg 20-50 µm	Muffle furnace	56.0 ±1.0	
	Mg 20-50 µm	TGA	56.1 ±0.9	
	Chamber residue	TGA	4.3 ±0.1	92%
	Cyclone residue	TGA	1.6 ±0.7	97%
n°3	Mg 20-50 µm	Muffle furnace	n.m	
	Mg 20-50 µm	TGA	55.6 ±0.5	
	Chamber residue	TGA	4.5 ±0.9	92%
	Cyclone residue	TGA	4.0 ±0.5	93%
n°5	Mg 50-70 µm	Muffle furnace	63.1 ±0.7	
	Mg 50-70 µm	TGA	61.1 ±0.4	
	Chamber residue	TGA	5.6 ±0.6	91%
	Cyclone residue	TGA	2.0 ±0.6	96%
n°6	Mg 50-70 µm	Muffle furnace	63.1 ±0.7	
	Mg 50-70 µm	TGA	61.1 ±0.4	
	Chamber residue	TGA	2.2 ±0.4	98%
	Cyclone residue	TGA	2.0 ±0.4	98%
n°7	Mg 50-70 µm	Muffle furnace	63.1 ±0.7	
	Mg 50-70 µm	TGA	61.1 ±0.4	
	Chamber residue	TGA	4.5 ±0.9	91%
	Cyclone residue	TGA	2.3 ±0.6	96%

Table 3: Magnesium injected and collected. Normalization using MgO equivalence

Combustion - fuel	Magnesium injected		Chamber residue		Cyclone residue		Exhaust particles (data from ELPI)	MgO collected/ MgO injected
	Sum (g)	MgO equivalent (g)	Collected (g)	MgO equivalent (g)	Collected (g)	MgO equivalent (g)	Considered as MgOequivalent(g)	Percentage (%)
n°1 - Mg 20-50µm	19.9	31.0	17.7	17.8	2.0	2.0	0.1	64.0
n°2 - Mg 20-50µm	20.5	32.0	18.8	19.6	7.6	7.7	0.1	85.7
n°3 - Mg 20-50µm	23.1	35.9	17.7	18.5	6.6	6.8	0.2	70.9
n°5 - Mg 50-70µm	34.0	55.5	35.6	37.7	10.8	11.0	1.5	90.5
n°6 - Mg 50-70µm	35.5	57.9	37.0	39.1	11.8	12.0	4.5	96.1
n°7 - Mg 50-70µm	35.5	57.9	37.7	38.6	12.8	13.1	3.3	94.9

From the experiments presented here, it clearly appears that the magnesium injected in the combustion chamber is oxidized. Therefore the injection flow rate may be used for a rough estimation of the heat released by combustion. Considering an enthalpy for MgO formation equal to 601 kJ mol⁻¹ [41], the combustion power developed by the magnesium oxidation ranges from 3.0 to 5.0 kW in our experimental conditions.

419

420 3.3 The overall ignition and combustion process: gaseous and TSP emissions

421 An example of two gaseous emissions patterns is shown in figures 10.a and 10.b. Data
 422 from ELPI software were synchronized with an analysis of the gaseous emissions (CO₂, O₂,
 423 NO, NO₂). Focusing on figure 10.a (combustion experiment n°2, Mg 20-50µm fraction), the
 424 oxy-acetylene combustion stage may be correlated to CO₂ in the exhaust. From 30 s to about
 425 60 s, the oxy-acetylene flame is ignited and stabilized, before Mg is injected. Then the Mg
 426 mass flow rate is increased, ending with the nominal mass flow rate. During this stage, the
 427 CO₂ concentration and the NO_x mole fraction increase up to around 18 vol% and 1900 ppm,
 428 respectively. The NO_x emissions are mainly composed of NO (66%). At about 70s, the oxy-
 429 acetylene flame is shut down as soon as a stable Mg/air flame is obtained. The magnesium
 430 combustion is coupled with a strong and progressive increase of NO_x emissions (up to about
 431 6500 ppm), while CO₂ emissions go down. These important NO_x emissions may be attributed
 432 to the high level of temperature in the oxy-acetylene flame and in the further Mg flame. The
 433 smaller NO_x level observed in the presence of the oxy-acetylene flame could be attributed to
 434 NO_x reburning, as already observed by Cai et al.[42].

435

436

437

438 Figure 10.a: Gaseous (O₂, CO₂, NO, NO₂) and Total Suspended Particles (TSP from ELPI)
 439 emissions during the ignition and stable combustion process (combustion run n°2 with Mg
 440 fraction from 20 to 50 µm).

441

Figure 10.b: Gaseous (O_2 , CO_2 , NO , NO_2) and Total Suspended Particles (TSP from ELPI) emissions during the ignition and stable combustion process (combustion run n°6 with Mg fraction from 50 to 70 μm).

TSP particles emissions are also observed during the Mg combustion. They may be considered as a solid combustion by-product (MgO). After this stable Mg/air flame stage, Mg injection was stopped and the inlet gas was immediately switched to pure N_2 , in order to inert the combustion chamber and the cyclone. One can observe in figure 10.a that the mole fraction of the different gases and the TSP concentration go down during this stage. Similar gaseous and TSP emissions have also been monitored for Mg 50-70 μm fraction (combustion experiment n°6, figure 10.b). TSP emissions are lower for the experiments with 20-50 μm samples (from 1.3 to 3.0 $g/(N)m^3$), than for the experiments with 50-70 μm samples (from 17.1 to 35.2 $g/(N)m^3$), as the highest Mg fraction is certainly more susceptible to emit bigger particles. In the same way, NO emissions are lower for the 50-70 μm samples (from 670 to 1540 $mg/(N)m^3$), than for the 20-50 μm samples (from 3350 to 5000 $mg/(N)m^3$). A similar trend is observed for NO_2 emissions. The NO_x emissions measured during the Mg combustion stage (50-70 μm samples) are 2 to 4 times greater than those measured at the output of a Diesel engine. Mg particles burn according to a well-known $\tau \sim d^2$ law, where τ is the burning time and d is the magnesium particle size [16,18,19,24]. For particles with larger diameter, as in the case for the 50-70 μm fraction, the heat released by combustion will occur over a longer time length in the combustion process. The gas temperature will therefore be both uniform and lower in the combustion chamber. Thermal NO_x formation is consequently reduced.

Considering equation (1), the molar ratio between Mg and O_2 should be equal to 2. The experimental molar flow rates of Mg injected and O_2 consumed are reported in table 4. The ratio Mg/O_2 is close to 2, for most of the experimental runs. It ranges from 1.9 (run n°2, with the fraction 20-50 μm) to 2.3 (run n°7, with the fraction 50-70 μm). This confirms that under

the experimental conditions used in this study, the combustion is quite complete. For the experiment n°3, the molar ratio is equal to 2.9, probably due to some leaks in the sampling lines.

Table 4: Dynamic flow rates of Mg fuel and O₂ consumed, with NO_x and TSP emissions

	Duration of stable Mg/Air flamme (s)	Mg injected (mol/h)	O ₂ used (mol/h)	(mol Mg) / (mol O ₂)	NO (mg/Nm ³)	NO ₂ (mg/Nm ³)	TSP (g/N m ³)
n°2 - Mg 20-50µm	113	18.0 ±0.4	9.4 ±0.1	1.9	5000 ±210	2800 ±240	1.3
n°3 - Mg 20-50µm	125	18.0 ±0.4	6.3 ±0.1	2.9	3350 ±180	1700 ±210	1.6
n°5 - Mg 50-70µm	126	28.0 ±0.6	12.9 ±0.1	2.2	1540 ±150	350 ±190	17.1
n°6 - Mg 50-70µm	140	28.5 ±0.6	13.5 ±0.1	2.1	1100 ±140	250 ±190	35.2
n°7 - Mg 50-70µm	125	30.0 ±0.6	13.1 ±0.1	2.3	670 ±130	<300	26.1

The mass size distributions (figure 11.a and 11.b) of the PM emissions during the runs n°2 (Mg 20-50 µm) and n°6 (Mg 50-70 µm) show that the particles emitted from the stable Mg/air flame are mostly larger than 1 µm (respectively 85 wt% and 95 wt%). The particle number size distributions are bimodal. The number size distribution of the particles emitted during the combustion of Mg 20-50 µm fraction is positioned at 0.08 µm, with a second mode occurring at a smaller diameter. For the combustion of the Mg 50-70 µm fraction, the number size distribution is more widespread around 0.3 µm for the dominant mode and around 0.04 µm for the lower one. The PM emitted from Mg combustion are also bigger than the ones emitted from Diesel combustion, which are divided in two modes: the accumulation one characterized by a size from 0.05 to 0.5 µm and the nuclei mode with a size lower than 0.05 µm. Particle mass in the accumulation mode contributes to about 90% of the total particle mass but to only 10-30% of their total number [43] .

Figure 11.a: Particle number and mass size distributions during the stable Mg/Air flame (combustion run n°2 with Mg sifted fraction from 20 to 50 μm)

Figure 11.b: Particle number and mass size distributions during the stable Mg/Air flame (combustion run n°6 with Mg sifted fraction from 50 to 70 μm)

4. Conclusions

Innovative ways of energy production and storage have to be explored in order to cope with fossil fuel scarcity and non-constant energy production by renewable energies, such as wind turbines or photovoltaic cells. This study introduces the feasibility of magnesium energy release at a pilot scale (from 3.0 to 5.0 kW). Magnesium/air stable flames (lasting about 2 minutes) were obtained from raw magnesium powder sifted and sized in two fractions: 20-50 μm and 50-70 μm . Combustion completion ratios ranged from 91 to 100 %. Acceptable molar ratios between Mg injected and O_2 consumed were obtained (from 1.8 to 2.3), corresponding to the stoichiometric combustion.

NO_x and fine particles emissions are issues to be considered if Mg/Air technique is used as a future alternative energy source. As shown in the present study, NO_x emissions are higher for the 20-50 μm fraction (NO average of $4300 \pm 200 \text{ mg}/(\text{N})\text{m}^3$) than for the 50-70 μm fraction (NO average of $1100 \pm 140 \text{ mg}/(\text{N})\text{m}^3$). The level of NO_x emission is 10 times higher for Mg/air combustion than for a conventional Diesel engine but it should be lowered by an optimization of the combustion conditions in the boiler. Moreover different after-treatment systems are already available for NO_x abatement and could be efficiently used at the gas exhaust of the Mg/air combustion chamber: Selective Non-Catalytic Reduction (SNCR) [44,45] or Selective Catalytic Reduction (SCR) [46,47] for instance. Concerning the PM and especially fine and ultrafine particles, the results presented in this study show that most of the particles are trapped in the cyclone. The Total suspended particles (TSP) emissions at the cyclone outflow are very high (from 1 to 35 $\text{g}/(\text{N})\text{m}^3$), but should be considerably lowered as mainly large particles - 85 to 97 wt% bigger than 1 μm - are produced. Hence it should be possible to trap such particles using a combination of cyclones in order to decrease their cut-off diameter. Moreover some other devices can also be considered such as particulate filters, electro-filters, etc. Consequently NO_x emission and PM emissions should not be seen as an issue for the development of Mg/air combustion in boilers. This will be considered in further works with two successive steps: first the optimization of the

combustion chamber in order to decrease the level of pollutants emitted and second the development of appropriated after-treatment systems.

5. Acknowledgments

The authors thank Prof. G. Trouvé (GRE, UHA), for valuable expertise and discussion about fine and ultrafine characterization and Prof. O. Haeberlé and Prof. A. Dieterlen from the MIPS laboratory (UHA) for their kind welcome to the optical microscope.

6. References

- [1] Quan P, Leephakpreeda T. Assessment of wind energy potential for selecting wind turbines: An application to Thailand. *Sustain Energy Technol Assess* 2015;11:17–26. doi:10.1016/j.seta.2015.05.002.
- [2] Price T, Bunn J, Probert D, Hales R. Wind-energy harnessing: Global, national and local considerations. *Appl Energy* 1996;54:103–79. doi:10.1016/0306-2619(95)00073-9.
- [3] Sathiamoorthy M, Probert SD. The integrated Severn barrage complex: Harnessing tidal, wave and wind power. *Appl Energy* 1994;49:17–46. doi:10.1016/0306-2619(94)90055-8.
- [4] Numbi BP, Malinga SJ. Optimal energy cost and economic analysis of a residential grid-interactive solar PV system- case of eThekweni municipality in South Africa. *Appl Energy* 2017;186, Part 1:28–45. doi:10.1016/j.apenergy.2016.10.048.
- [5] Hirvonen J, Kayo G, Cao S, Hasan A, Sirén K. Renewable energy production support schemes for residential-scale solar photovoltaic systems in Nordic conditions. *Energy Policy* 2015;79:72–86. doi:10.1016/j.enpol.2015.01.014.
- [6] Han B, Steen III SM, Mo J, Zhang F-Y. Electrochemical performance modeling of a proton exchange membrane electrolyzer cell for hydrogen energy. *Int J Hydrog Energy* 2015;40:7006–16. doi:10.1016/j.ijhydene.2015.03.164.
- [7] Gubler L. Polymer Design Strategies for Radiation-Grafted Fuel Cell Membranes. *Adv Energy Mater* 2014;4:n/a – n/a. doi:10.1002/aenm.201300827.
- [8] Li Y, Shi Y, Mehio N, Tan M, Wang Z, Hu X, et al. More sustainable electricity generation in hot and dry fuel cells with a novel hybrid membrane of Nafion/nano-silica/hydroxyl ionic liquid. *Appl Energy* 2016;175:451–8. doi:10.1016/j.apenergy.2016.03.075.
- [9] Coniglio L, Coutinho JAP, Clavier J-Y, Jolibert F, Jose J, Mokbel I, et al. Biodiesel via supercritical ethanolysis within a global analysis “feedstocks-conversion-engine” for a sustainable fuel alternative. *Prog Energy Combust Sci* 2014;43:1–35. doi:10.1016/j.peccs.2014.03.001.
- [10] Shkolnikov EI, Zhuk AZ, Vlaskin MS. Aluminum as energy carrier: Feasibility analysis and current technologies overview. *Renew Sustain Energy Rev* 2011;15:4611–23. doi:10.1016/j.rser.2011.07.091.
- [11] Lomba R, Bernard S, Gillard P, Mounaïm-Rousselle C, Halter F, Chauveau C, et al. Comparison of Combustion Characteristics of Magnesium and Aluminum Powders. *Combust Sci Technol* 2016;188:1857–77. doi:10.1080/00102202.2016.1211871.
- [12] Lutgens FK, Tarbuck EJ, Tasa DG. *Essentials of Geology*. 12 edition. Boston: Pearson; 2014.
- [13] Capus JM. Chapter 3 - Global and regional markets for metal powders 2001–2010. *Met. Powders Fourth Ed.*, Oxford: Elsevier Science; 2005, p. 57–120.
- [14] Yuasa S, Fukuchi A. Ignition and combustion of magnesium in carbon dioxide streams. *Symp Int Combust* 1994;25:1587–94. doi:10.1016/S0082-0784(06)80804-0.

- [15] Corcoran A, Mercati S, Nie H, Milani M, Montorsi L, Dreizin EL. Combustion of fine aluminum and magnesium powders in water. *Combust Flame* 2013;160:2242–50. doi:10.1016/j.combustflame.2013.04.019.
- [16] Law CK, Williams FA. Combustion of magnesium particles in oxygen-inert atmospheres. *Combust Flame* 1974;22:383–405. doi:10.1016/0010-2180(74)90053-4.
- [17] Dreizin EL, Hoffmann VK. Constant pressure combustion of aerosol of coarse magnesium particles in microgravity. *Combust Flame* 1999;118:262–80. doi:10.1016/S0010-2180(98)00144-8.
- [18] Aly Y, Dreizin EL. Ignition and combustion of Al-Mg alloy powders prepared by different techniques. *Combust Flame* 2015;162:1440–7. doi:10.1016/j.combustflame.2014.11.010.
- [19] Wang S, Corcoran AL, Dreizin EL. Combustion of magnesium powders in products of an air/acetylene flame. *Combust Flame* 2015;162:1316–25. doi:10.1016/j.combustflame.2014.10.016.
- [20] Cassel HM, Liebman I. Combustion of magnesium particles I. *Combust Flame* 1962;6:153–6. doi:10.1016/0010-2180(62)90084-6.
- [21] Markstein GH. Combustion of metals. *AIAA J* 1963;1:550–62. doi:10.2514/3.1595.
- [22] Legrand B, Marion M, Chauveau C, Gokalp I, Shafirovich E. Ignition and Combustion of Levitated Magnesium and Aluminum Particles in Carbon Dioxide. *Combust Sci Technol* 2001;165:151–74. doi:10.1080/00102200108935830.
- [23] Dreizin EL, Berman CH, Vicenzi EP. Condensed-phase modifications in magnesium particle combustion in air. *Combust Flame* 2000;122:30–42. doi:10.1016/S0010-2180(00)00101-2.
- [24] Dreizin EL. Metal-based reactive nanomaterials. *Prog Energy Combust Sci* 2009;35:141–67. doi:10.1016/j.pecs.2008.09.001.
- [25] Salih OS, Ou H, Sun W, McCartney DG. A review of friction stir welding of aluminium matrix composites. *Mater Des* 2015;86:61–71. doi:10.1016/j.matdes.2015.07.071.
- [26] Kimura M, Fuji A, Shibata S. Joint properties of friction welded joint between pure magnesium and pure aluminium with post-weld heat treatment. *Mater Des* 2015;85:169–79. doi:10.1016/j.matdes.2015.06.175.
- [27] Chen S, Jiang X. Microstructure evolution during magnetic pulse welding of dissimilar aluminium and magnesium alloys. *J Manuf Process* 2015;19:14–21. doi:10.1016/j.jmapro.2015.04.001.
- [28] Haynes H, Asmatulu R. Chapter 7 - Nanotechnology Safety in the Aerospace Industry. *Nanotechnol. Saf.*, Amsterdam: Elsevier; 2013, p. 85–97.
- [29] Czerwinski F. Controlling the ignition and flammability of magnesium for aerospace applications. *Corros Sci* 2014;86:1–16. doi:10.1016/j.corsci.2014.04.047.
- [30] Eckelman MJ, Ciacci L, Kavlak G, Nuss P, Reck BK, Graedel TE. Life cycle carbon benefits of aerospace alloy recycling. *J Clean Prod* 2014;80:38–45. doi:10.1016/j.jclepro.2014.05.039.
- [31] M'Saoubi (1) R, Axinte (1) D, Soo (2) SL, Nobel C, Attia (1) H, Kappmeyer (3) G, et al. High performance cutting of advanced aerospace alloys and composite materials. *CIRP Ann - Manuf Technol* 2015;64:557–80. doi:10.1016/j.cirp.2015.05.002.
- [32] Bergthorson JM, Goroshin S, Soo MJ, Julien P, Palecka J, Frost DL, et al. Direct combustion of recyclable metal fuels for zero-carbon heat and power. *Appl Energy* 2015;160:368–82. doi:10.1016/j.apenergy.2015.09.037.
- [33] Nakata T, Silva D, Rodionov M. Application of energy system models for designing a low-carbon society. *Prog Energy Combust Sci* 2011;37:462–502. doi:10.1016/j.pecs.2010.08.001.
- [34] Mazloomi K, Gomes C. Hydrogen as an energy carrier: Prospects and challenges. *Renew Sustain Energy Rev* 2012;16:3024–33. doi:10.1016/j.rser.2012.02.028.

- [35] Davidson CI, Phalen RF, Solomon PA. Airborne Particulate Matter and Human Health: A Review. *Aerosol Sci Technol* 2005;39:737–49. doi:10.1080/02786820500191348.
- [36] Giere R, Querol X. Solid Particulate Matter in the Atmosphere. *Elements* 2010;6:215–22. doi:10.2113/gselements.6.4.215.
- [37] Chen Y, Hobbs BF, Hugh Ellis J, Crowley C, Joutz F. Impacts of climate change on power sector NO_x emissions: A long-run analysis of the US mid-atlantic region. *Energy Policy* 2015;84:11–21. doi:10.1016/j.enpol.2015.04.013.
- [38] González A, Riba J-R, Rius A, Puig R. Optimal sizing of a hybrid grid-connected photovoltaic and wind power system. *Appl Energy* 2015;154:752–62. doi:10.1016/j.apenergy.2015.04.105.
- [39] Keskinen J, Pietarinen K, Lehtimäki M. Electrical low pressure impactor. *J Aerosol Sci* 1992;23:353–60. doi:10.1016/0021-8502(92)90004-F.
- [40] Yetter RA, Risha GA, Son SF. Metal particle combustion and nanotechnology. *Proc Combust Inst* 2009;32:1819–38. doi:10.1016/j.proci.2008.08.013.
- [41] Cox JD, Wagman DD, Medvedev VA. *Codata Key Values for Thermodynamics*. 1st edition. New York: Hemisphere Publishing Corporation; 1989.
- [42] Cai L, Shang X, Gao S, Wang Y, Dong L, Xu G. Low-NO_x coal combustion via combining decoupling combustion and gas reburning. *Fuel* 2013;112:695–703. doi:10.1016/j.fuel.2011.12.028.
- [43] Petrović VS, Janković SP, Tomić MV, Jovanović ZS, Knežević DM. The Possibilities for Measurement and Characterization of Diesel Engine Fine Particles - a Review. *Therm Sci* 2011;15:915–38. doi:10.2298/TSCI110509092P.
- [44] Mahmoudi S, Baeyens J, Seville JPK. NO_x formation and selective non-catalytic reduction (SNCR) in a fluidized bed combustor of biomass. *Biomass Bioenergy* 2010;34:1393–409. doi:10.1016/j.biombioe.2010.04.013.
- [45] Daood SS, Javed MT, Gibbs BM, Nimmo W. NO_x control in coal combustion by combining biomass co-firing, oxygen enrichment and SNCR. *Fuel* 2013;105:283–92. doi:10.1016/j.fuel.2012.06.087.
- [46] Schuler A, Votsmeier M, Kiwic P, Gieshoff J, Hautpmann W, Drochner A, et al. NH₃-SCR on Fe zeolite catalysts – From model setup to NH₃ dosing. *Chem Eng J* 2009;154:333–40. doi:10.1016/j.cej.2009.02.037.
- [47] Pârvulescu VI, Grange P, Delmon B. Catalytic removal of NO. *Catal Today* 1998;46:233–316. doi:10.1016/S0920-5861(98)00399-X.